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IN THE UNITED STATES PATENT AND TRADE MARK OFFICE

In re Application of Masumi SUETSUGU et al.

Serial No. 10/664,355

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Group Art Unit : 1752

Examiner : Rosemary E. ASHTON

## NEGATIVE TYPE RESIST COMPOSITION

\* \* \* \* \*

### DECLARATION

I, Masumi SUETSUGU, residing at 2-3-1,  
Hotarugaikenaka-machi, Toyonaka-shi, Osaka, 560-0033, Japan,  
declare and say:

that I was graduated from Master Course of Graduate School of  
Engineering, Yokohama National University in March 1990.

Since April 1990 to the present, I have been employed by  
Sumitomo Chemical Co., Ltd., assignee of the above-identified  
application, and, since 1990 to the present, I have been engaged in  
research and development in the field of photoresist;

that I am one of the inventors of the invention of the  
above-identified application; and

that in order to show the unexpected results obtained by the negative  
type resist composition of the present invention, I beg to submit the following

experimental data which have been obtained under my supervision:

## Experiments

In the examples, % and parts showing content and use amount are by weight unless otherwise stated. Weight-average molecular weight ( $M_w$ ) and degree of polydispersion ( $M_w/M_n$ ) are values measured by gel permeation chromatography using polystyrene as a standard.

### 1. Synthesis of partially etherified poly(p-hydroxystyrene) with 1-ethoxyethyl group (1)

Into a reaction vessel, were charged 21.0 parts of poly(p-hydroxystyrene) ["VP-2500", manufactured by Nippon Soda, having a weight average molecular weight of 4,000 and a distribution of 1.14], and 84 parts of acetone, and they were stirred to make a solution. To this solution were charged 12.7 parts of anhydrous potassium carbonate and 8.2 parts of ethyl iodide, and the temperature was elevated so that the mixture reached the reflux state. Then the solution was kept at the reflux state for 15 hours. After adding methyl isobutyl ketone, the organic layer was washed with an aqueous oxalic acid solution, then washed with ion-exchanged water. The organic layer after washing was concentrated to 44 parts, combined with 130 parts of propylene glycol monomethyl ether acetate and further concentrated to 63 parts. The solid content of the concentrate measured by weight-loss on heating was 32.33 % by weight. By  $^1\text{H-NMR}$  measurement, it was confirmed that the resin was a copolymer in which 27.5% of hydroxyl groups in poly(p-hydroxystyrene) was ethyletherified. The resin was referred to as RESIN A1.

### 2. Synthesis of partially etherified poly(p-hydroxystyrene) with 1-ethoxyethyl

group (2)

The procedure in 1. above was repeated except that the amount of anhydrous potassium carbonate was 15.5 parts and that of ethyl iodide was 10.9 parts. As the result, a solution in which the solid content of the concentrate measured by weight-loss on heating was 33.66% by weight was obtained. By <sup>1</sup>H-NMR measurement, it was confirmed that the resin was a copolymer in which 38.6% of hydroxyl groups in poly(p-hydroxystyrene) was ethyletherified. The resin was referred to as RESIN A2.

### 3. Example 1 and Comparative Examples 1 to 3

11 parts of RESIN A1, 47 parts of RESIN A2, 42 parts of poly(p-hydroxystyrene) ["VP-2500"], 11 parts of N-(isopropylsulfonyloxy)succinimide as an acid generator, 5 parts of hexamethoxymethylmelamine as a crosslinking agent and 0.1 part of a basic compound defined in Table 1 were dissolved using propylene glycol monomethyl ether acetate as dilution solvent, further, the mixtures were filtrated through fluorine resin filter having pore diameter of 0.2 μm, to prepare resist solution.

On a silicon wafer treated with hexamethyldisilazane, the above-mentioned resist solution was applied using a rotation applicator so that the film thickness after prebake drying was 0.56 μm. Prebake after application of the resist solution was conducted at 100°C for 60 seconds on a hot plate. The wafer carrying thus formed resist film was exposed to line and space pattern using a KrF excimer laser exposure [ "NSR 2205EX12B" manufactured by Nikon Corp., NA=0.55, σ=0.8]. Then, post exposure bake was conducted at 105°C or 100°C for 60 seconds on a hot plate, further, puddle development was conducted with a 2.38% tetramethylammonium hydroxide aqueous solution for 60 seconds. The pattern after the development was observed by a scanning type electron microscope, and effective sensitivity, resolution, profile and temperature

dependency were checked according to the following methods. The results are shown in Table 2.

**Effective Sensitivity:** It is represented by exposure amount when line and space pattern of 0.25  $\mu\text{m}$  is 1:1.

**Resolution:** It is represented by the minimum size of separated 1:1 line and space pattern at the exposure amount fixed as Effective sensitivity.

**Profile:** Expressed with  $\bigcirc$  when the line-and-space pattern cross section after development is nearly rectangle and  $\times$  when the top is round or the cross section is inversely tapered.

**Temperature Dependency:** The line section width of 0.25 $\mu\text{m}$  line-and-space pattern is measured when the resist is exposed at the exposure amount of effective sensitivity and post exposure bake is carried out at 105 $^{\circ}\text{C}$  and that at 100 $^{\circ}\text{C}$  is also measured. Based on the widths at 105 $^{\circ}\text{C}$  and at 100 $^{\circ}\text{C}$ , dimensional changes per 1 $^{\circ}\text{C}$  are calculated.

Table 2

No.	Basic Compound	ES [mJ/cm <sup>2</sup> ]	RES [ $\mu\text{m}$ ]	PRO	TD [nm/ $^{\circ}\text{C}$ ]
Exp.1	1,3-di(4-pyridyl)propane	34	0.16	$\bigcirc$	7
Comp Exp.1	2,6-diphenylpyridine	12	0.17	$\times$	25
Comp Exp.2	2-n-propylpyridine	12	0.18	$\times$	29
Comp Exp.3	2-phenylpyridine	12	0.18	$\times$	26

ES: Effective Sensitivity

RES: Resolution

PRO: Profile

TD: Temperature Dependency

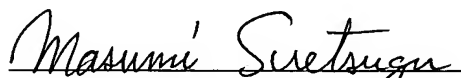
A composition obtained in Example 1, which corresponds to the present composition and contains a basic compound of the amended formula (I) having two pyridine ring in its molecule, gives patterns with smaller temperature dependency of the pattern dimensions after exposure and having excellent

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resolution and profile compared to the compositions which contain a basic compound having only one pyridine ring in its molecule.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United State Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 28<sup>th</sup> day of July 2005.

  
Masumi SUETSUGU